

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
8 June 2006 (08.06.2006)

PCT

(10) International Publication Number  
**WO 2006/060206 A1**

(51) International Patent Classification:  
C01F 7/02 (2006.01) C01F 7/44 (2006.01)

(21) International Application Number:  
PCT/US2005/042028

(22) International Filing Date:  
18 November 2005 (18.11.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
10/992,477 18 November 2004 (18.11.2004) US

(71) Applicant (for all designated States except US): SAINT-  
GOBAIN CERAMICS & PLASTICS, INC. [US/US]; 1  
New Bond Street, Box Number 15138, Worcester, Massa-  
chusetts 01615-0138 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): BAUER, Ralph  
[CA/CA]; 6913 Cumberland Court, Niagara Falls, Ontario  
L2H 4R6 (CA). YENER, Doruk [TR/US]; Apartement 10,  
473 Boston Turnpike, Shrewsbury, Massachusetts 01545  
(US). SKOWRON, Margaret [US/US]; 557 74th Street,  
Niagara Falls, New York 14304 (US). BARNES, Martin  
[US/US]; 1944 Youngstown-lockport Road, Ransomville,  
New York 14131 (US). BRANDES, Alan [US/US]; 88  
Central Tree Road, Rutland, Massachusetts 01543 (US).

(74) Agents: BUJOLD, Michael, J. et al.; DAVIS & BUJOLD,  
P.L.L.C., 500 North Commercial Street, Fourth Floor, Man-  
chester, New Hampshire 03101-1151 (US).

(81) Designated States (unless otherwise indicated, for every  
kind of national protection available): AE, AG, AL, AM,  
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,  
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,  
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,  
KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV,  
LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI,  
NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG,  
SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US,  
UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every  
kind of regional protection available): ARIPO (BW, GH,  
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,  
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,  
FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT,  
RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,  
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Declarations under Rule 4.17:**

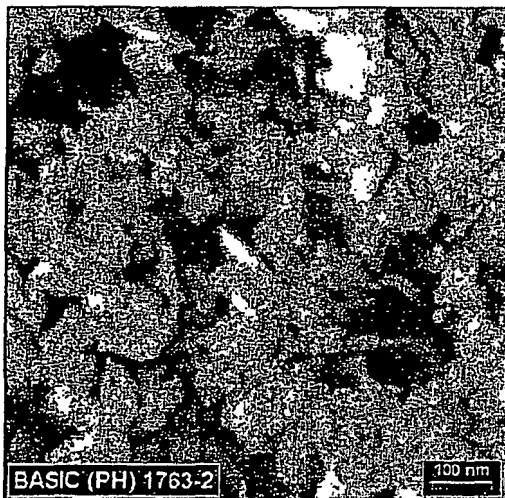
- as to applicant's entitlement to apply for and be granted a  
patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the  
earlier application (Rule 4.17(iii))

**Published:**

- with international search report
- before the expiration of the time limit for amending the  
claims and to be republished in the event of receipt of  
amendments

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: TRANSITIONAL ALUMINA PARTICULATE MATERIALS HAVING CONTROLLED MORPHOLOGY AND PRO-  
CESSING FOR FORMING SAME



(57) Abstract: An alumina particulate material is dis-  
closed, including particles comprising transitional alu-  
mina having an aspect ratio of not less than 3:1 and an  
average particle size of not less than 75nm. Also dis-  
closed are fabrication techniques based on seeded pro-  
cessing pathways.

TRANSITIONAL ALUMINA PARTICULATE MATERIALS HAVING  
CONTROLLED MORPHOLOGY AND PROCESSING FOR FORMING SAME

Ralph Bauer  
Doruk Yener  
Margaret Skowron  
Martin Barnes  
Alan Brandes

BACKGROUND

Field of the Disclosure

[0001] The present invention generally relates to transitional alumina particulate material and processes for forming same. More specifically, the present invention relates to transitional alumina particulate material having novel morphological features.

Description of the Related Art

[0002] Aluminous materials have been used in quite a large and varying scope of industrial applications and technologies, from single crystal applications focusing on optical and optoelectronic applications, to polycrystalline abrasive grains used in free abrasives, bonded abrasives, and coated abrasives, for example. Aluminous materials are generally polymorphic, and may include various hydrated forms such as boehmite and gibbsite. Among the various alumina materials, alumina, or aluminum oxide, is a particular material of interest. In various industrial applications, alumina is employed in its hardest and most stable allotropic state, alpha-alumina. However, the transitional forms of alumina, which include gamma, delta, and theta have gained commercial interest as these phases have desirable properties, such as desirable hardness and surface area characteristics that make transitional alumina of great interest in areas as diverse as printing inks and catalyst carriers.

[0003] Currently available transitional aluminas are typically processed by heat treating transitional alumina precursor materials such as gibbsite, boehmite, or bayerite to the desired phase transformation temperature. Other techniques rely on direct synthesis via a wet chemical processing, such as through hydrolysis of aluminum alkoxide. Current techniques often suffer from poor yield, high expense, and/or limited flexibility to form new morphologies that may be of interest in emerging markets based on exploitation of transitional aluminas.

[0004] Accordingly, as should be clear, a need exists in the art for transitional aluminas that have novel morphological features. In addition to the interest in creating new materials, processing technology enabling the formation of such materials needs to be developed as well. In this regard, such processing technology is desirably cost effective, is relatively straightforward to control, and provides high yields.

#### SUMMARY

[0005] According to one embodiment, alumina particulate material contains particles comprising transitional alumina having an aspect ratio of not less than 3:1 and an average particle size of not less than about 110 nm and not greater than 1000 nm.

[0006] According to another embodiment, alumina particulate material, containing mainly seeded needle-shaped particles comprising transitional alumina having an aspect ratio of not less than 3:1, a secondary aspect ratio of not greater than 3:1, and an average particle size of not less than about 75 nm.

[0007] According to another embodiment, alumina particulate material, containing mainly seeded platy-shaped particles comprising transitional alumina having an aspect ratio of not less than 3:1, a secondary aspect ratio of not less than 3:1, and an average particle size of not less than about 125 nm.

[0008] According to another embodiment, a method for forming alumina particulate material calls for providing a boehmite precursor and boehmite seeds in a suspension, heat treating the suspension to convert the boehmite precursor into boehmite particulate

material; and calcining the boehmite particulate material to transform the boehmite particulate material into transitional alumina particulate material.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The present disclosure may be better understood, and its numerous features and advantages made apparent to those skilled in the art by referencing the accompanying drawings.

[0010] FIG. 1 is an SEM micrograph showing platelet shaped transitional alumina.

[0011] FIG. 2 is an SEM micrograph showing needle shaped transitional alumina.

[0012] FIG. 3 is an SEM micrograph showing ellipsoid shaped transitional alumina.

[0013] The use of the same reference symbols in different drawings indicates similar or identical items.

#### DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

[0014] According to an embodiment of the present invention, a powder in the form of a transitional alumina particulate material is formed through a seeded processing pathway. Processing typically involves heat treatment of a transitional alumina precursor into transitional alumina, in form of gamma, delta, or theta alumina, or combinations thereof. The transitional alumina is generally a mass of particulate material, composed of particles that may be fully dispersed, partially agglomerated, or fully agglomerated. In the dry form, the particulate material may be described as a powder. The process typically makes use of boehmite as the transitional alumina precursor, which is processed through the above-noted seeded processing pathway. In more detail, processing includes providing a boehmite precursor and boehmite seeds in a suspension, and heat treating (such as by hydrothermal treatment) the suspension (alternatively sol or slurry) to convert the boehmite precursor into boehmite particulate material formed of particles or crystallites. Heat treatment is then carried out to the boehmite particulate material to

effect polymorphic transformation into transitional alumina. According to a particular aspect, the boehmite particulate material has a relatively elongated morphology, described generally herein in terms of aspect ratio and described in more detail below. In addition, the morphological features associated with the boehmite are preserved in the final transitional alumina particulate material.

[0015] The term "boehmite" is generally used herein to denote alumina hydrates including mineral boehmite, typically being  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  and having a water content on the order of 15%, as well as psuedoboehmite, having a water content higher than 15%, such as 20-38% by weight. It is noted that boehmite (including psuedoboehmite) has a particular and identifiable crystal structure, and accordingly unique X-ray diffraction pattern, and as such, is distinguished from other aluminous materials including other hydrated aluminas such as ATH (aluminum trihydroxide) a common precursor material used herein for the fabrication of boehmite particulate materials.

[0016] The aspect ratio, defined as the ratio of the longest dimension to the next longest dimension perpendicular to the longest dimension, is generally not less than 2:1, and preferably not less than 3:1, 4:1, or 6:1. Indeed, certain embodiments have relatively elongated particles, such as not less than 8:1, 10:1, and in some cases, not less than 14:1. With particular reference to needle-shaped particles, the particles may be further characterized with reference to a secondary aspect ratio defined as the ratio of the second longest dimension to the third longest dimension. The secondary aspect ratio is generally not greater than 3:1, typically not greater than 2:1, or even 1.5:1, and oftentimes about 1:1. The secondary aspect ratio generally describes the cross-sectional geometry of the particles in a plane perpendicular to the longest dimension. It is noted that since the term aspect ratio is used herein to denote the ratio of the longest dimension to the next longest dimension, it may be referred as the primary aspect ratio.

[0017] According to another embodiment, the boehmite can be platey or platelet-shaped particles generally have an elongated structure having the aspect ratios described above in connection with the needle-shaped particles. However, platelet-shaped particles generally have opposite major surfaces, the opposite major surfaces being generally

planar and generally parallel to each other. In addition, the platelet-shaped particles may be characterized as having a secondary aspect ratio greater than that of needle-shaped particles, generally not less than about 3:1, such as not less than about 6:1, or even not less than 10:1. Typically, the shortest dimension or edge dimension, perpendicular to the opposite major surfaces or faces, is generally less than 50 nanometers, such as less than about 40 nanometers, or less than about 30 nanometers.

[0018] Morphology of the boehmite particulate material may be further defined in terms of particle size, more particularly, average particle size. Here, the seeded boehmite particulate material, that is, boehmite formed through a seeding process (described in more detail below) has a relatively fine particle or crystallite size. Generally, the average particle size is not greater than about 1000 nanometers, and fall within a range of about 100 to 1000 nanometers. Other embodiments have even finer average particle sizes, such as not greater than about 800 nanometers, 750 nanometers, 600 nanometers, 500 nanometers, 400 nanometers, and even particles having an average particle size smaller than 300 nanometers, representing a fine particulate material. In the context of fine particulate material, embodiments were shown to have a particle size smaller than 250 nanometers, such as not greater than 225 nanometers. One range for average particle size lies within a range of 150 to 200 nanometers. Due to process constraints of certain embodiments, the smallest average particle size is generally limited, such as not less than about 75 nanometers, 100 nanometers (particularly in the case of platy particulate material a minimum particle size of 110 nanometers), 125 nanometers, or 135 nanometers.

[0019] As used herein, the "average particle size" is used to denote the average longest or length dimension of the particles. Due to the elongated morphology of the particles, conventional characterization technology is generally inadequate to measure average particle size, since characterization technology is generally based upon an assumption that the particles are spherical or near-spherical. Accordingly, average particle size was determined by taking multiple representative samples and physically measuring the particle sizes found in representative samples. Such samples may be taken by various characterization techniques, such as by scanning electron microscopy (SEM). The term

average particle size also denotes primary particle size, related to the individually identifiable particles, whether dispersed or agglomerated forms. Of course, agglomerates have a comparatively larger average particle size, and the present disclosure does not focus on agglomerate sizing.

[0020] The present seeded boehmite particulate material has been found to have a fine average particle size, while oftentimes competing non-seeded based technologies are generally incapable of providing such fine average particle sizes. In this regard, it is noted that oftentimes in the literature, reported particle sizes are not set forth in the context of averages as in the present specification, but rather, in the context of nominal range of particle sizes derived from physical inspection of samples of the particulate material. Accordingly, the average particle size will lie within the reported range in the prior art, generally at about the arithmetic midpoint of the reported range, for the expected Gaussian particle size distribution. Stated alternatively, while non-seeded based technologies may report fine particle size, such fine sizing generally denotes the lower limit of an observed particle size distribution and not average particle size.

[0021] Likewise, in a similar manner, the above-reported aspect ratios generally correspond to the average aspect ratio taken from representative sampling, rather than upper or lower limits associated with the aspect ratios of the particulate material. Oftentimes in the literature, reported particle aspect ratios are not set forth in the context of averages as in the present specification, but rather, in the context of nominal range of aspect ratios derived from physical inspection of samples of the particulate material. Accordingly, the average aspect ratio will lie within the reported range in the prior art, generally at about the arithmetic midpoint of the reported range, for the expected Gaussian particle morphology distribution. Stated alternatively, while non-seeded based technologies may report aspect ratio, such data generally denotes the lower limit of an observed aspect ratio distribution and not average aspect ratio.

[0022] In addition to aspect ratio and average particle size of the particulate material, morphology of the particulate material may be further characterized in terms of specific surface area. Here, the commonly available BET technique was utilized to measure

specific surface area of the particulate material. According to embodiments herein, the boehmite particulate material has a relatively high specific surface area, generally not less than about  $10 \text{ m}^2/\text{g}$ , such as not less than about  $50 \text{ m}^2/\text{g}$ ,  $70 \text{ m}^2/\text{g}$ , or not less than about  $90 \text{ m}^2/\text{g}$ . Since specific surface area is a function of particle morphology as well as particle size, generally the specific surface area of embodiments was less than about  $400 \text{ m}^2/\text{g}$ , such as less than about  $350$  or  $300 \text{ m}^2/\text{g}$ . Specific ranges for surface area are about  $75 \text{ m}^2/\text{g}$  to  $200 \text{ m}^2/\text{g}$ .

[0023] Turning to the details of the processes by which the boehmite particulate material (forming a transitional alumina precursor, or feedstock material) may be manufactured, generally ellipsoid, needle, or platelet-shaped boehmite particles are formed from a boehmite precursor, typically an aluminous material including bauxitic minerals, by hydrothermal treatment as generally described in the commonly owned patent described above, US Patent 4,797,139. More specifically, the boehmite particulate material may be formed by combining the boehmite precursor and boehmite seeds in suspension, exposing the suspension (alternatively sol or slurry) to heat treatment to cause conversion of the raw material into boehmite particulate material, further influenced by the boehmite seeds provided in suspension. Heating is generally carried out in an autogenous environment, that is, in an autoclave, such that an elevated pressure is generated during processing. The pH of the suspension is generally selected from a value of less than 7 or greater than 8, and the boehmite seed material has a particle size finer than about 0.5 microns. Generally, the seed particles are present in an amount greater than about 1% by weight of the boehmite precursor (calculated as  $\text{Al}_2\text{O}_3$ ), and heating is carried out at a temperature greater than about  $120^\circ\text{C}$ , such as greater than about  $125^\circ\text{C}$ , or even greater than about  $130^\circ\text{C}$ , and at a pressure that is autogenously generated, typically around 30 psi.

[0024] The particulate material may be fabricated with extended hydrothermal conditions combined with relatively low seeding levels and acidic pH, resulting in preferential growth of boehmite along one axis or two axes. Longer hydrothermal treatment may be used to produce even longer and higher aspect ratio of the boehmite particles and/or larger particles in general.

[0025] Following heat treatment, such as by hydrothermal treatment, and boehmite conversion, the liquid content is generally removed, such as through an ultrafiltration process or by heat treatment to evaporate the remaining liquid. Thereafter, the resulting mass is generally crushed, such to 100 mesh. It is noted that the particulate size described herein generally describes the single crystallites formed through processing, rather than the aggregates which may remain in certain embodiments (e.g., for those products that call for and aggregated material).

[0026] According to data gathered by the present inventors, several variables may be modified during the processing of the boehmite raw material, to effect the desired morphology. These variables notably include the weight ratio, that is, the ratio of boehmite precursor to boehmite seed, the particular type or species of acid or base used during processing (as well as the relative pH level), and the temperature (which is directly proportional to pressure in an autogenous hydrothermal environment) of the system.

[0027] In particular, when the weight ratio is modified while holding the other variables constant, the shape and size of the particles forming the boehmite particulate material are modified. For example, when processing is carried at 180°C for two hours in a 2 weight % nitric acid solution, a 90:10 ATH:boehmite seed ratio forms needle-shaped particles (ATH being a species of boehmite precursor). In contrast, when the ATH:boehmite seed ratio is reduced to a value of 80:20, the particles become more elliptically shaped. Still further, when the ratio is further reduced to 60:40, the particles become near-spherical. Accordingly, most typically the ratio of boehmite precursor to boehmite seeds is not less than about 60:40, such as not less than about 70:30 or 80:20. However, to ensure adequate seeding levels to promote the fine particulate morphology that is desired, the weight ratio of boehmite precursor to boehmite seeds is generally not greater than about 98:2. Based on the foregoing, an increase in weight ratio generally increases aspect ratio, while a decrease in weight ratio generally decreased aspect ratio.

[0028] Further, when the type of acid or base is modified, holding the other variables constant, the shape (e.g., aspect ratio) and size of the particles are affected. For example,

when processing is carried out at 180°C for two hours with an ATH:boehmite seed ratio of 90:10 in a 2 weight % nitric acid solution, the synthesized particles are generally needle-shaped, in contrast, when the acid is substituted with HCl at a content of 1 weight % or less, the synthesized particles are generally near spherical. When 2 weight % or higher of HCl is utilized, the synthesized particles become generally needle-shaped. At 1 weight % formic acid, the synthesized particles are platelet-shaped. Further, with use of a basic solution, such as 1 weight % KOH, the synthesized particles are platelet-shaped. If a mixture of acids and bases is utilized, such as 1 weight % KOH and 0.7 weight % nitric acid, the morphology of the synthesized particles is platelet-shaped. Noteworthy, the above weight % values of the acids and bases are based on the solids content only of the respective solid suspensions or slurries, that is, are not based on the total weight % of the total weight of the slurries.

[0029] Suitable acids and bases include mineral acids such as nitric acid, organic acids such as formic acid, halogen acids such as hydrochloric acid, and acidic salts such as aluminum nitrate and magnesium sulfate. Effective bases include, for example, amines including ammonia, alkali hydroxides such as potassium hydroxide, alkaline hydroxides such as calcium hydroxide, and basic salts.

[0030] Still further, when temperature is modified while holding other variables constant, typically changes are manifested in particle size. For example, when processing is carried out at an ATH:boehmite seed ratio of 90:10 in a 2 weight % nitric acid solution at 150°C for two hours, the crystalline size from XRD (x-ray diffraction characterization) was found to be 115 Angstroms. However, at 160°C the average particle size was found to be 143 Angstroms. Accordingly, as temperature is increased, particle size is also increased, representing a directly proportional relationship between particle size and temperature.

[0031] According to embodiments described herein, a relatively powerful and flexible process methodology may be employed to engineer desired morphologies into the precursor boehmite product. Of particular significance, embodiments utilize seeded processing resulting in a cost-effective processing route with a high degree of process

control which may result in desired fine average particle sizes as well as controlled particle size distributions. The combination of (i) identifying and controlling key variables in the process methodology, such as weight ratio, acid and base species and temperature, and (ii) seeding-based technology is of particular significance, providing repeatable and controllable processing of desired boehmite particulate material morphologies.

[0032] While the foregoing has focused on boehmite production, which forms the feedstock material or transitional alumina precursor material, a particular aspect of the present invention involves further processing of the precursor material into transitional alumina. Here, the boehmite precursor is heat treated by calcination at a temperature sufficient to cause transformation into a transitional phase alumina, or a combination of transitional phases. Typically, calcination or heat treatment is carried out at a temperature greater than about 250°C, but lower than 1100°C. At temperatures less than 250°C, transformation into the lowest temperature form of transitional alumina, gamma alumina, typically will not take place. At temperatures greater than 1100°C, typically the precursor will transform into the alpha phase, which is to be avoided to obtain transitional alumina particulate material. According to certain embodiments, calcination is carried out at a temperature greater than 400°C, such as not less than about 450°C. The maximum calcination temperature may be less than 1050 or 1100°C, these upper temperatures usually resulting in a substantial proportion of theta phase alumina, the highest temperature form of transitional alumina.

[0033] Other embodiments are calcined at a temperature lower than 950°C, such as within a range of 750 to 950°C to form a substantial content of delta alumina. According to particular embodiments, calcination is carried out at a temperature less than about 800°C, such as less than about 775°C or 750°C to effect transformation into a predominant gamma phase.

[0034] Calcination may be carried out in various environments including controlled gas and pressure environments. Because calcination is generally carried out to effect phase changes in the precursor material and not chemical reaction, and since the resulting

material is predominantly an oxide, specialized gaseous and pressure environments need not be implemented except for most desired transitional alumina end products.

[0035] However, typically, calcination is carried out for a controlled time period to effect repeatable and reliable transformation from batch to batch. Here, most typically shock calcination is not carried out, as it is difficult to control temperature and hence control phase distribution. Accordingly, calcination times typically range from about 0.5 minutes to 60 minutes typically, 1 minute to 15 minutes.

[0036] Generally, as a result of calcination, the particulate material is mainly (more than 50 wt%) transitional alumina. More typically, the transformed particulate material was found to contain at least 70 wt%, typically at least 80 wt%, such as at least 90 wt% transitional alumina. The exact makeup of transitional alumina phases may vary according to different embodiments, such as a blend of transitional phases, or essentially a single phase of a transitional alumina (e.g., at least 95 wt%, 98wt%, or even up to 100 wt% of a single phase of a transitional alumina).

[0037] According to one particular feature, the morphology of the boehmite feedstock material is largely maintained in the final, as-formed transitional alumina. Accordingly, desirable morphological features may be engineered into the boehmite according to the foregoing teaching, and those features preserved. For example embodiments have been shown to retain at least the specific surface area of the feedstock material, and in some cases, increase surface area by amount of at least 8%, 10%, 12%, 14% or more. Since morphology is largely preserved in the final product, the foregoing description in connection with morphological features of the boehmite may be applicable to the transitional alumina particulate material as well.

[0038] For example, the aspect ratio of the transitional alumina particulate material is generally not less than 2:1; and preferably not less than 3:1, 4:1, or 6:1. Indeed, certain embodiments have relatively elongated particles, such as not less than 8:1, 10:1, and in some cases, not less than 14:1. With particular reference to needle-shaped particles, the secondary aspect ratio is generally not greater than 3:1, typically not greater than 2:1, or even 1.5:1, and oftentimes about 1:1. The secondary aspect ratio generally describes the

cross-sectional geometry of the particles in a plane perpendicular to the longest dimension.

[0039] Platey or platelet-shaped transitional alumina particles generally have an elongated structure having the aspect ratios described above in connection with the needle-shaped particles. However, platelet-shaped particles generally have opposite major surfaces, the opposite major surfaces being generally planar and generally parallel to each other. In addition, the platelet-shaped particles may be characterized as having a secondary aspect ratio greater than that of needle-shaped particles, generally not less than about 3:1, such as not less than about 6:1, or even not less than 10:1. Typically, the shortest dimension or edge dimension, perpendicular to the opposite major surfaces or faces, is generally less than 50 nanometers, such as less than about 40 nanometers, or less than about 30 nanometers.

[0040] Further, the average particle size of the transitional alumina particulate material is generally not greater than about 1000 nanometers, and fall within a range of about 75 to 750 nanometers. Other embodiments have even finer average particle sizes, such as not greater than about 600 nanometers, 500 nanometers, 400 nanometers, 300 nanometers, and even particles having an average particle size smaller than 275 nanometers, representing a fine particulate material. In the context of fine particulate material, embodiments were shown to have a particle size smaller than 250 nanometers, such as not greater than 225 nanometers. One range for average particle size lies within a range of 150 to 200 nanometers. Due to process constraints of certain embodiments, the smallest average particle size is generally limited, such as not less than about 75 nanometers, 100 nanometers, (particularly in the case of platy particulate material a minimum particle size of 110 nanometers), 125 nanometers, or 135 nanometers.

[0041] As above, the term "average particle size" is used to denote the average longest or length dimension of the particles. Due to the elongated morphology of the particles, conventional characterization technology is generally inadequate to measure average particle size, since characterization technology is generally based upon an assumption that the particles are spherical or near-spherical. Accordingly, average particle size was

determined by taking multiple representative samples and physically measuring the particle sizes found in representative samples. Such samples may be taken by various characterization techniques, such as by scanning electron microscopy (SEM). It is noted that oftentimes in the literature, reported particle sizes are not set forth in the context of averages as in the present specification, but rather, in the context of nominal range of particle sizes derived from physical inspection of samples of the particulate material. Accordingly, the average particle size will lie within the reported range in the prior art, generally at about the arithmetic midpoint of the reported range, for the expected Gaussian particle size distribution. The term average particle size also denotes primary particle size, related to the individually identifiable particles, whether dispersed or agglomerated forms. Of course, agglomerates have a comparatively larger average particle size, and the present disclosure does not focus on agglomerate sizing.

[0042] Likewise, in a similar manner, the above-reported aspect ratios generally correspond to the average aspect ratio taken from representative sampling, rather than upper or lower limits associated with the aspect ratios of the particulate material. Oftentimes in the literature, reported particle aspect ratios are not set forth in the context of averages as in the present specification, but rather, in the context of nominal range of aspect ratios derived from physical inspection of samples of the particulate material. Accordingly, the average aspect ratio will lie within the reported range in the prior art, generally at about the arithmetic midpoint of the reported range, for the expected Gaussian particle morphology distribution. Stated alternatively, while non-seeded based technologies may report aspect ratio, such data generally denotes the lower limit of an observed aspect ratio distribution and not average aspect ratio.

[0043] In addition to aspect ratio and average particle size of the particulate material, morphology of the particulate material may be further characterized in terms of specific surface area. Here, the commonly available BET technique was utilized to measure specific surface area of the transitional alumina particulate material. According to embodiments herein, the particulate material has a relatively high specific surface area, generally not less than about  $10 \text{ m}^2/\text{g}$ , such as not less than about  $50 \text{ m}^2/\text{g}$ ,  $70 \text{ m}^2/\text{g}$ , or not less than about  $90 \text{ m}^2/\text{g}$ . Since specific surface area is a function of particle morphology

as well as particle size, generally the specific surface area of embodiments was less than about 400 m<sup>2</sup>/g, such as less than about 350 or 300 m<sup>2</sup>/g. Specific ranges for surface area are about 75 m<sup>2</sup>/g to 200 m<sup>2</sup>/g.

[0044] Particular significance is attributed to the seeded processing pathway, as not only does seeded processing to form the transitional alumina precursor allow for tightly controlled morphology of the precursor (which is largely preserved in the final product), but also the seeded processing route is believed to manifest desirable physical properties in the final product, including compositional, morphological, and crystalline distinctions over transitional alumina formed by conventional, non-seeded processing pathways..

[0045] Example 1, Plate-shaped particle synthesis

[0046] An autoclave was charged with 7.42 lb. of Hydral 710 aluminum trihydroxide purchased from Alcoa; 0.82 lb of boehmite obtained from SASOL under the name-- Catapal B pseudoboehmite; 66.5 lb of deionized water; 0.037 lb potassium hydroxide; and 0.18 lb of 22wt% nitric acid. The boehmite was pre-dispersed in 5 lb of the water and 0.18 lb of the acid before adding to the aluminum trihydroxide and the remaining water and potassium hydroxide.

[0047] The autoclave was heated to 185°C. over a 45 minute period and maintained at that temperature for 2 hours with stirring at 530 rpm. An autogenously generated pressure of about 163 psi was reached and maintained. Thereafter the boehmite dispersion was removed from the autoclave. After autoclave the pH of the sol was about 10. The liquid content was removed at a temperature of 65°C. The resultant mass was crushed to less than 100 mesh. The SSA of the resultant powder was about 62 m<sup>2</sup>/g.

[0048] This material was calcined at 530°C for 5 minutes to transform into gamma alumina. After calcination, the material was confirmed to be 100% gamma alumina due to X-Ray diffraction Rietveld analysis. The specific surface area of the sample was 100.7 m<sup>2</sup>/g. See Fig. 1.

[0049] Example 2, Needle-shaped particle synthesis

[0050] An autoclave was charged with 250 g of Hydral 710 aluminum trihydroxide purchased from Alcoa; 25 g of boehmite obtained from SASOL under the name--Catapal B pseudoboehmite; 1000 g of deionized water; and 34.7 g of 18% nitric acid. The boehmite was pre-dispersed in 100 g of the water and 6.9 g of the acid before adding to the aluminum trihydroxide and the remaining water and acid.

[0051] The autoclave was heated to 180°C. over a 45 minute period and maintained at that temperature for 2 hours with stirring at 530 rpm. An autogenously generated pressure of about 150 psi was reached and maintained. Thereafter the boehmite dispersion was removed from the autoclave. After autoclave the pH of the sol was about 3. The liquid content was removed at a temperature of 95°C. The resultant mass was crushed to less than 100 mesh. The SSA of the resultant powder was about 120 m<sup>2</sup>/g.

[0052] This material was calcined at 530 °C for 5 min to transform into gamma alumina. After calcination, it was confirmed to be 100% gamma alumina due to X-Ray diffraction Rietveld analysis. The specific surface area of the sample was 145.1 m<sup>2</sup>/g. See Fig. 2.

[0053] Example 3, Ellipsoid shaped particle synthesis

[0054] An autoclave was charged with 220 g of Hydral 710 aluminum trihydroxide purchased from Alcoa; 55 g of boehmite obtained from SASOL under the name--Catapal B pseudoboehmite; 1000 g of deionized water; and 21.4 g of 18% nitric acid. The boehmite was pre-dispersed in 100 g of the water and 15.3 g of the acid before adding to the aluminum trihydroxide and the remaining water and acid.

[0055] The autoclave was heated to 172°C. over a 45 minute period and maintained at that temperature for 3 hours with stirring at 530 rpm. An autogenously generated pressure of about 120 psi was reached and maintained. Thereafter the boehmite dispersion was removed from the autoclave. After autoclave the pH of the sol was about 4. The liquid content was removed at a temperature of 95°C. The resultant mass was crushed to less than 100 mesh. The SSA of the resultant powder was about 135 m<sup>2</sup>/g.

[0056] This material was calcined at 530°C for 5 minutes to transform into gamma alumina. After calcination, it was confirmed to be 100% gamma alumina due to X-Ray diffraction Rietveld analysis. The specific surface area of the sample 167.8 m<sup>2</sup>/g. See Fig. 3.

[0057] Aspects of the present invention enable utilization of the boehmite particulate material in a wide variety of applications, including applications that are not particularly well suited for boehmite, such as in applications requiring higher hardness and/or involve high temperature processing, such as melt processing of fluorinated polymers. Properties of flame retardance, UV protection, weatherability, chemical resistance, thermal conductivity, and electrical resistance make the present transitional alumina a significant industrial material. Other uses include implementation as an additive to paper, as an ink absorbent in inkjet printing, as a catalyst, as a filtration media, or as an abrasive in demanding chemical mechanical polishing used in the electronics industry.

[0058] While the invention has been illustrated and described in the context of specific embodiments, it is not intended to be limited to the details shown, since various modifications and substitutions can be made without departing in any way from the scope of the present invention. For example, additional or equivalent substitutes can be provided and additional or equivalent production steps can be employed. As such, further modifications and equivalents of the invention herein disclosed may occur to persons skilled in the art using no more than routine experimentation, and all such modifications and equivalents are believed to be within the scope of the invention as defined by the following claims.

## WHAT IS CLAIMED IS:

1. Alumina particulate material, comprising:  
particles comprising transitional alumina having an aspect ratio of not less than 3:1 and an average particle size of not less than about 110 nm and not greater than 1000 nm.
2. The particulate material of claim 1, wherein the transitional alumina is selected from the group consisting of gamma alumina, delta alumina, and theta alumina.
3. The particulate material of claim 2, wherein the transitional alumina is selected from the group consisting of gamma alumina and delta alumina.
4. The particulate material of claim 3, wherein the transitional alumina is gamma alumina.
5. The particulate material of claim 1, wherein the particles comprise at least 70 wt% transitional alumina.
6. The particulate material of claim 5, wherein the particles comprise at least 80 wt% transitional alumina.
7. The particulate material of claim 6, wherein the particles comprise at least 90 wt% transitional alumina.
8. The particulate material of claim 7, wherein the transitional alumina is selected from the group consisting of gamma alumina, delta alumina, and theta alumina.
9. The particulate material of claim 8, wherein the transitional alumina is selected from the group consisting of gamma alumina and delta alumina.

10. The particulate material of claim 1, wherein the aspect ratio is not less than about 5:1.
11. The particulate material of claim 10, wherein the aspect ratio is not less than about 6:1.
12. The particulate material of claim 11, wherein the aspect ratio is not less than about 8:1.
13. The particulate material of claim 12, wherein the aspect ratio is not less than about 10:1.
14. The particulate material of claim 1, wherein the average particle size is not less than 125 nm.
15. The particulate material of claim 14, wherein the average particle size is not less than about 135 nm.
16. The particulate material of claim 1, wherein the average particle size is not greater than about 750 nm.
17. The particulate material of claim 16, wherein the average particle size is not greater than about 500 nm.
18. The particulate material of claim 17, wherein the average particle size is not greater than about 300 nm.
19. The particulate material of claim 18, wherein the average particle size is within a range of about 150 nm to 200 nm.
20. The particulate material of claim 1, wherein the particles have a platy shape and a secondary aspect ratio of not less than 3:1.

21. The particulate material of claim 20, wherein the secondary aspect ratio is not less than 6:1.

22. The particulate material of claim 21, wherein the secondary aspect ratio is not less than 10:1.

23. The particulate material of claim 1, wherein the particles have a needle shape and a secondary aspect ratio of not greater than 3:1.

24. The particulate material of claim 20, wherein the secondary aspect ratio is not greater than 2:1.

25. The particulate material of claim 21, wherein the secondary aspect ratio is not greater than 1.5:1.

26. The particulate material of claim 1, having a specific surface area not less than about 50 m<sup>2</sup>/g.

27. The particulate material of claim 26, having a specific surface area not less than about 70 m<sup>2</sup>/g.

28. The particulate material of claim 1, having a specific surface area not greater than about 400 m<sup>2</sup>/g.

29. The particulate material of claim 28, having a specific surface area not greater than about 300 m<sup>2</sup>/g.

30. The particulate material of claim 1, wherein the alumina particulate material is seeded alumina particulate material.

31. The particulate material of claim 1, consisting essentially of said particles.

32. Alumina particulate material, comprising mainly:  
seeded needle-shaped particles comprising transitional alumina having an aspect ratio of not less than 3:1, a secondary aspect ratio of not greater than 3:1, and an average particle size of not less than about 75 nm.

33. The particulate material of claim 32, wherein the secondary aspect ratio is not greater than 2:1.

34. Alumina particulate material, comprising mainly:  
seeded platy-shaped particles comprising transitional alumina having an aspect ratio of not less than 3:1, a secondary aspect ratio of not less than 3:1, and an average particle size of not less than about 125 nm.

35. The alumina particulate material of claim 34, wherein the secondary aspect ratio is not less than 6:1.

36. A method for forming alumina particulate material, comprising:  
providing a boehmite precursor and boehmite seeds in a suspension;  
heat treating the suspension to convert the boehmite precursor into boehmite particulate material; and  
calcining the boehmite particulate material to transform the boehmite particulate material into transitional alumina particulate material.

37. The method of claim 36, wherein heat treating is carried out at a temperature greater than about 120°C.

38. The method of claim 36, wherein heat treating is carried out at an autogenous pressure .

39. The method of claim 36, wherein a weight ratio of boehmite precursor to boehmite seeds is not less 60:40.

40. The method of claim 39, wherein the weight ratio is not less than 80:20.
41. The method of claim 40, wherein a weight ratio of boehmite precursor to boehmite seeds is not greater than 98:2.
42. The method of claim 36, wherein the average particle size of the transitional alumina particulate material is not less than 75 nm.
43. The method of claim 42, wherein the average particle size is not less than about 100 nm.
44. The method of claim 36, wherein the average particle size is not greater than about 300 nm.
45. The method of claim 44, wherein the average particle size is not greater than about 250 nm.
46. The method of claim 45, wherein the average particle size is not greater than about 225 nm.
47. The method of claim 46, wherein the average particle size is within a range of about 150 nm to 200 nm.
48. The method of claim 36, wherein the transitional alumina particulate material has a platy shape and a secondary aspect ratio of not less than 3:1.
49. The method of claim 48, wherein the secondary aspect ratio is not less than 6:1.
50. The method of claim 49, wherein the secondary aspect ratio is not less than 10:1.

51. The method of claim 36, wherein the transitional alumina particulate material has a needle shape and a secondary aspect ratio of not greater than 3:1.

52. The method of claim 51, wherein the secondary aspect ratio is not greater than 2:1.

53. The method of claim 52, wherein the secondary aspect ratio is not greater than 1.5:1.

54. The method of claim 36, wherein calcination is carried out to maintain morphology of the boehmite particulate material.

55. The method of claim 54, wherein the transitional alumina particulate has specific surface area that greater than that of the boehmite particulate material.

56. The method of claim 55, wherein the specific surface area of the transitional alumina particulate material is at least 8% greater than that of the boehmite particulate material.

57. The method of claim 55, wherein the specific surface area of the transitional alumina particulate material is not less than about 50 m<sup>2</sup>/g.

58. The method of claim 57, wherein the specific surface area of the transitional alumina particulate material is not less than about 70 m<sup>2</sup>/g.

59. The method of claim 55, wherein the specific surface area of the transitional alumina particulate material is not greater than about 400 m<sup>2</sup>/g.

60. The method of claim 59, wherein the specific surface area of the transitional alumina particulate material is not greater than about 300 m<sup>2</sup>/g.

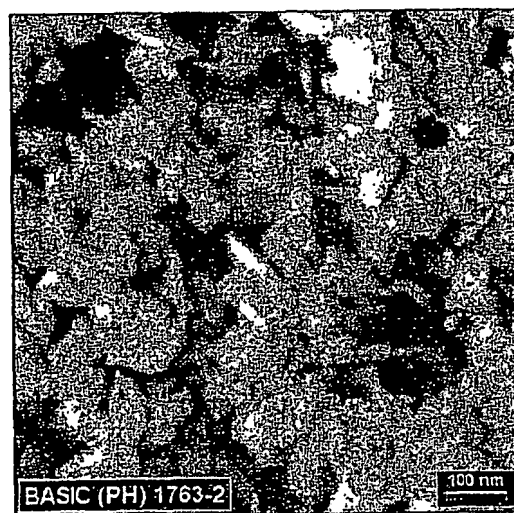


FIG. 1

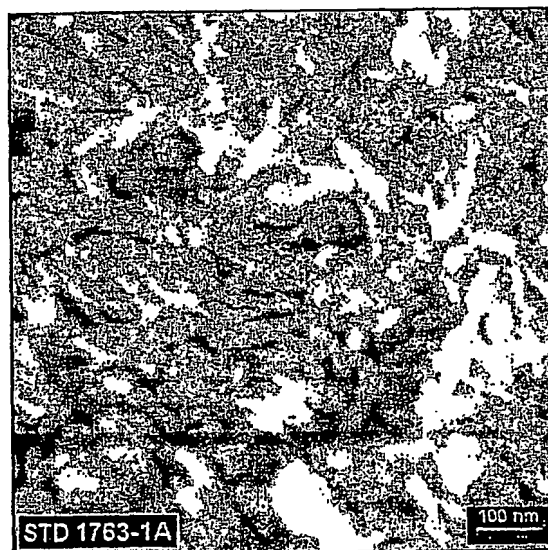


FIG. 2

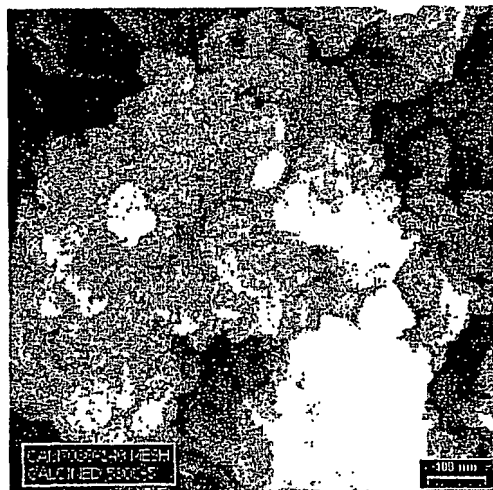


FIG. 3

A. CLASSIFICATION OF SUBJECT MATTER  
 INV. C01F7/02 C01F7/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 440 187 B1 (KASAI TOSHIO ET AL) 27 August 2002 (2002-08-27) claim 1; example 1	1-60
Y	EP 0 304 721 A (NORTON COMPANY) 1 March 1989 (1989-03-01) cited in the application the whole document	1-60
	----- -/-- -----	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

\* & \* document member of the same patent family

Date of the actual completion of the international search

12 May 2006

Date of mailing of the international search report

19/05/2006

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Rhodes, K

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	BOCCACCINI A R ET AL: "Alumina ceramics based on seeded boehmite and electrophoretic deposition" CERAMICS INTERNATIONAL, ELSEVIER, AMSTERDAM, NL, vol. 28, no. 8, 2002, pages 893-897, XP004388719 ISSN: 0272-8842 1. Introduction 2. Experimental Procedure -----	36-60
P,A	WO 2005/100244 A (SAINT-GOBAIN CERAMICS & PLASTICS, INC; BAUER, RALPH; YENER, DORUK; SKO) 27 October 2005 (2005-10-27) the whole document -----	36-60

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6440187	B1	27-08-2002	DE 69910170 D1	11-09-2003
			DE 69910170 T2	03-06-2004
			EP 1044163 A1	18-10-2000
			WO 9935089 A1	15-07-1999
			TW 555696 B	01-10-2003
EP 0304721	A	01-03-1989	AU 595463 B2	29-03-1990
			AU 2045288 A	16-02-1989
			BR 8804056 A	02-05-1989
			CA 1302681 C	09-06-1992
			DE 3879584 D1	29-04-1993
			DE 3879584 T2	23-09-1993
			DK 447188 A	12-02-1989
			IN 170641 A1	25-04-1992
			JP 1069511 A	15-03-1989
			JP 2030766 C	19-03-1996
			JP 7061861 B	05-07-1995
			KR 9602622 B1	24-02-1996
			MX 164999 B	13-10-1992
			NO 883535 A	13-02-1989
			NZ 225586 A	26-07-1991
			US 4797139 A	10-01-1989
WO 2005100244	A	27-10-2005	NONE	